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## THE EFFECT OF INITIAL COMPONENTS ON THE SYNTHESIS OF FORSTERITE PRODUCED BY THE SOL-GEL METHOD

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The effect of the type of magnesium salts and the silicon-containing component on the synthesis and properties of forsterite powder synthesized by the sol-gel method are considered. It is established that the use of magnesium acetate significantly decreases the starting temperature of forsterite formation, and the amorphous type of silica is preferable as a silicon-containing component.

Forsterite materials, which have a relatively low sintering temperature (usually below 1400°C), a structure that remains stable in time and under heat treatment, substantial radiation resistance, and a high TCLE, are widely used in various fields of engineering, primarily, in electronic devices [1]. However, the development of dense fine-crystalline forsterite ceramics to a maximum extent implementing the advantages of forsterite is a complicated problem.

It is rather difficult to produce such ceramics by the standard technology involving preliminary synthesis of forsterite using natural materials and even more difficult using high-purity silicon and magnesium oxides. These ceramics are currently prepared from highly active powders produced by special chemical methods (USSR Inventor's Certificate No. 381644) [2]. However, many of these methods are complicated, expensive, and involve toxic reactants, which restricts their wide practical use.

The sol-gel technology, which has become widespread due to its simplicity and the accessibility of its reactants and equipment, is promising for the production of high-dispersion powders [3, 4]. The use of this method makes it possible to lower the temperature of the synthesis of ultradisperse powders of a complex composition and to control their morphology and the phase composition of the material.

Research carried out at the D. I. Mendeleev Russian Chemical Engineering University [5, 6] made it possible to develop the principles of an original sol-gel technology for various compounds, including those of a complex composition. The main principle of this technology consists of obtaining the sol of an intermediate product, in which the components of a synthesized compound are distributed in the form of a true or colloid solution, with subsequent gel forma-

tion and the transformation of the whole system into a xerogel. However, the specific techniques for producing active forsterite powder have not yet been developed, in particular, the effect of the initial components on the synthesis of powder and the yield of the product has not been studied.

The purpose of our study was to develop a technology of producing active forsterite powder based on the sol-gel method by studying the effect of magnesium salts and the silicon-bearing component on the synthesis and the properties of the forsterite powder.

The initial components for forsterite powder were crystal hydrates of magnesium compounds: chloride  $MgCl_2 \cdot 6H_2O$ , nitrate  $Mg(NO_3)_2 \cdot 6H_2O$ , sulfate  $MgSO_4 \cdot 7H_2O$ , acetate  $Mg(CH_3COO)_2 \cdot 4H_2O$ , and citrate  $Mg(C_6H_5O_7)$ . Amorphous silica filler (SF) and sol of  $SiO_2$  were selected as the silicon-bearing component. Saturated solutions of the initial components were mixed, taking into account possible calcination losses, considering the stoichiometry of forsterite.

To improve the gel formation, the mixtures were exposed for 1 day at room temperature. Next, the gel was dried for 5 h at a temperature of 120°C up to a complete transformation into a porous spongy xerogel. Based on the data in [2] indicating that the forsterite formation when synthesized from a xerogel proceeds at a temperature over 700°C and ends at 1200°C, the heat treatment of the xerogel was carried out within a temperature range of 600–1200°C with an interval of 200°C. The xerogel was heated at a rate of 300 K/h with a 2 h exposure at the final temperature.

The specifics of the formation of forsterite from the initial compounds were investigated using differential thermal, x-ray phase, petrographic, electron microscope, and spectral analysis. The specific surface area of the powders was determined based on the method of low-temperature nitrogen absorption (BET).

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In view of the possibility of formation of various compounds (from forsterite and to intermediate forms of magnesium silicates) and the individual behaviors of the initial components in heating of xerogels, the thermograms of different mixtures may vary significantly. In order to exclude the effects typical of the initial components in analyzing the thermograms of xerogels, the DTA of these components was performed separately.

The DTA curve of the silica filler exhibits only one thermal effect up to 1500°C, i.e., an endothermic effect (40 – 100°C) related to the loss of water adsorbed on its surface. Polymorphous transformations of  $\text{SiO}_2$  were not registered.

Polyvinyl alcohol starts melting with subsequent decomposition within a temperature interval of 30 – 630°C and especially intensely at 340 – 360°C. The endothermic effects at 350 and 440°C are related to the oxidation of the destruction products, and the exothermic effect at 630°C is related to the destruction of the oxidized residue.

The  $\text{SiO}_2$  sol in the temperature interval of 30 – 110°C loses the adsorbed water (an endothermic effect) and at 850 – 880°C undergoes a transformation of  $\alpha$ -quartz contained in the sol into  $\alpha$ -tridimitite (an exothermic effect).

The thermogram of  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  can be interpreted based on the data in [7]. The insignificant deviations of the temperature intervals obtained by us from the intervals in [7] are related to the different purity of the chlorides analyzed or the different heating rate. The loss of physically bonded water occurs within the temperature interval of 30 – 100°C; later on the crystal-hydrate water is removed in several stages: the first two molecules are lost within a temperature interval of 100 – 120°C (the data in [7] indicate 116.7 – 181.5°C), the second two molecules are lost in the interval of 170 – 210°C (181.5 – 240°C), another molecule in the interval of 240 – 260°C (240 – 285°C), and then the decomposition into hydroxychloride within a temperature interval of 290 – 310°C (over 285°C) and the formation of the oxide at temperatures exceeding 485°C (over 500°C).

Magnesium nitrate in heating loses water in several stages: the first stage within a temperature range of 75 – 90°C, the second in a range of 135 – 165°C (according to the data in [7] four molecules of water are removed at a temperature above 90°C). The two subsequent endothermic effects (355 – 390 and 400 – 460°C) are related to a further loss of water and the decomposition of the nitrate into magnesium oxide and nitrogen oxides, which is indicated in [7] as occurring at a temperature over of 300°C.

The loss of the physically bonded water in the thermogram of  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  is registered within a temperature range of 90 – 120°C; after that the chemically bonded water is removed in several stages: six molecules are removed in the temperature intervals of 145 – 160 and 196 – 205°C (according to [7], above 150°C), and the last molecule within the temperature interval of 300 – 350°C (320 – 330°C). The endothermic effect at temperatures of 1000 – 1080°C

(1100 – 1200°C) indicates the decomposition of anhydrous sulfate.

The difficulty of interpreting the processes occurring in organic salts of magnesium is related to the lack of detailed thermographic data from other researchers, therefore; our observations are of a hypothetical but highly probable nature.

The decomposition of  $\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$  occurs in several stages, which is evidenced by the endothermic effects within the temperature intervals of 65 – 90, 115 – 145, 305 – 315, and 335 – 365°C, of which the first ones are caused by the dehydration of salt, and the last effects are most probably caused by the rupture of the oxygen and hydrogen bonds in the acid residue. The exothermic effects are most perceptible within the intervals of 235 – 305 and 365 – 440°C, and superimposing on the endothermic effects makes them smoother. They are probably determined by the rupture of the carbon bonds in the acid residue. At a temperature above 510°C, no changes occur in the analyzed powder consisting of magnesium oxide.

A similar phenomenon, although with different quantitative parameters, occurs in the crystal hydrate of magnesium citrate. All effects related to the loss of water, the decomposition of citrate, and burning out of the organic component of the salt are shifted to a higher temperature range. Thus, the endothermic effects have the temperature intervals of 60 – 150 and 340 – 360°C. The exothermic effects manifested within the temperature ranges of 245 – 340 and 370 – 440°C point to gradual burning out of the organic component as the acid residue decomposes.

The thermal behavior of xerogels differs from the decomposition of individual salts and does not represent a simple superposition of the thermal curves of the initial components. Furthermore, the course of a xerogel thermogram is affected by burning out of polyvinyl alcohol, which weakens the endothermic effects within the range of the decomposition of burning of the alcohol. Moreover, it should be taken into account that xerogels in their preparation are dried for long time at 120°C; consequently, the processes typical of salt crystal hydrates heated to these temperatures are not manifested or are weakly manifested in the thermograms. It is significant as well that the processes of decomposition and of synthesis are virtually simultaneous. This may cause mutual cancellation of the effects.

The behavior of the xerogels based on the silica filler with various magnesium-containing components in heating is to a great extent determined by the type of these components.

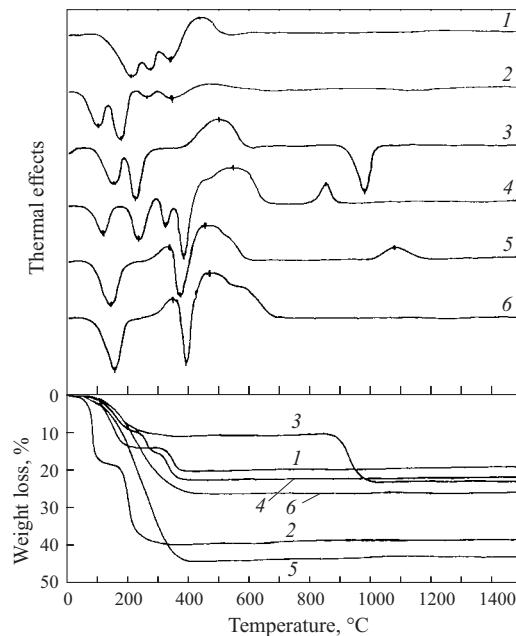
The xerogel based on magnesium chloride after losing crystal hydrate water in several stages within the temperature interval of 125 – 280°C starts decomposing with the formation of  $\text{MgO}$  at a temperature over 300°C (Fig. 1). The decomposition of xerogel produces disaggregated forsterite powder with a particle size up to 1  $\mu\text{m}$ . The powder particles at this moment have an identical refractive index in the whole volume, but with increasing temperature the homoge-

neity decreases. According to the x-ray phase analysis data, the first peaks correlated with forsterite appear at a temperature of 800°C, and at 1000°C the forsterite quantity reaches 80 – 90%. However, the exothermic effect corresponding to the forsterite-formation reaction is missing from the specified temperature range on the thermogram, which is probably related to the high rate of heating of the xerogel sample. According to the electron microscope analysis, the most homogeneous powder with respect to size is formed at a temperature of 1000°C, and as the temperature increases, the particle size grows.

The synthesis of forsterite based on magnesium nitrate occurs less intensely than in the first case. Thus, the xerogel based on  $Mg(NO_3)_2 \cdot 6H_2O$  decomposes within the temperature interval of 50 – 180°C with the loss of physically and chemically bonded water (Fig. 1). The two other endothermic effects indicate the decomposition of nitrate. However, according to the petrographic analysis data, the decomposition is not completed and 5 – 7% non-decomposed magnesium nitrate persists even at a temperature of 800°C. The rest is comprised of solid solutions with a forsterite lattice. An increase in the temperature to 1200°C results in an increasing quantity of the fine-dispersion phase of forsterite, and the excess of  $SiO_2$  is equal to 10%.

The forsterite-formation processes in the xerogel based on magnesium sulfate are sufficiently active at a temperature below the temperature of decomposition of the main volume of  $MgSO_4$  (below 980°C), which is indicated by the data of the x-ray phase and petrographic analysis. Thus, at a temperature of 900°C the amount of forsterite with a crystal size below 1  $\mu m$  reaches 70 – 75%, and the amount of the enstatite phase ( $MgO \cdot SiO_2$ ) constitutes about 15%. As the temperature grows to 1200°C, the amount of forsterite and the transitional forsterite forms increases and reaches 100%.

In the xerogel based on magnesium acetate, the loss of physically and chemically bonded water starts at a temperature above 90°C. The endothermic effects at 305 – 320 and 350 – 380°C (Fig. 1) are determined by the decomposition of magnesium salt. Simultaneously, polyvinyl alcohol is removed from the xerogel. The exothermic effect at 850°C is related to the formation of forsterite. However, the data of the x-ray and petrographic analysis point to the formation of 80% forsterite with a crystal size up to 2  $\mu m$  already at 600°C. Therefore, the fact that the exothermic effect is registered only at a temperature of 850°C is most probably related to the high rate of heating of the sample. At 600°C, apart from the forsterite crystals,  $MgO$  is present in the form of aggregates up to 20 – 25  $\mu m$ . It should also be noted that the lattice of the forsterite crystals is substantially deformed. As the temperature grows from 600 to 1200°C, the amount of the emerging forsterite grows, which is corroborated by the increased height of the peaks in the diffraction patterns. In this process, not only does the size of the forsterite crystals grow up to 4  $\mu m$ , but due to the high activity of the powder, it starts sintering and produces intercrystalline porosity up to

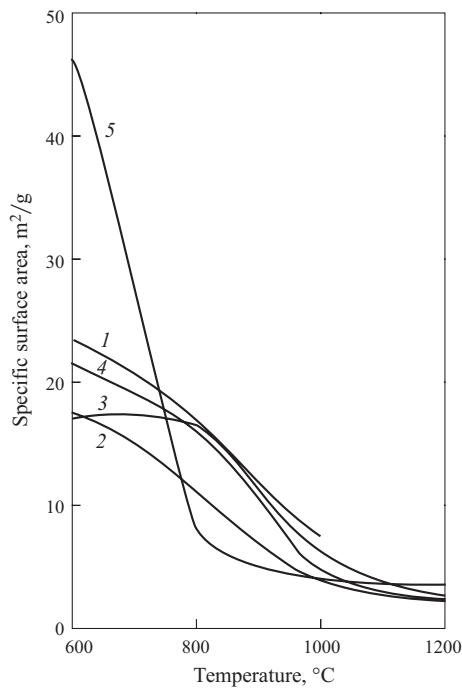


**Fig. 1.** Differential thermograms and weight-loss curves of xerogels based on  $MgCl_2 \cdot 6H_2O$  and amorphous SF (1),  $Mg(NO_3)_2 \cdot 6H_2O$  and SF (2),  $MgSO_4 \cdot 7H_2O$  and SF (3),  $Mg(CH_3COO_2) \cdot 4H_2O$  and SF (4),  $Mg_3(C_6H_5O_7)_2$  and SF (5), and  $Mg_3(C_6H_5O_7)_2$  and  $SiO_2$  sol (6).

2  $\mu m$  in size. Judging from the electron microscope analysis, the powder with the most homogenous particle size is formed at a temperature of 800°C.

The formation of forsterite in the xerogel based on magnesium citrate is less intense and proceeds at higher temperatures than in the case of magnesium acetate, which is indicated by the presence of an exothermic effect related to the formation of forsterite at a temperature of 1075°C (Fig. 1). This is substantiated by the data of the petrographic and x-ray phase analysis. Thus, after a synthesis at 600°C, the powder contains 50% forsterite with a distorted forsterite lattice and the rest is represented by intermediate phases. An increase in the temperature to 1200°C increases the quantity of forsterite up to 85%; however, well-formed forsterite crystals constitute only 25%. The remaining 15% is represented by  $SiO_2$  both in the bonded and in the free state.

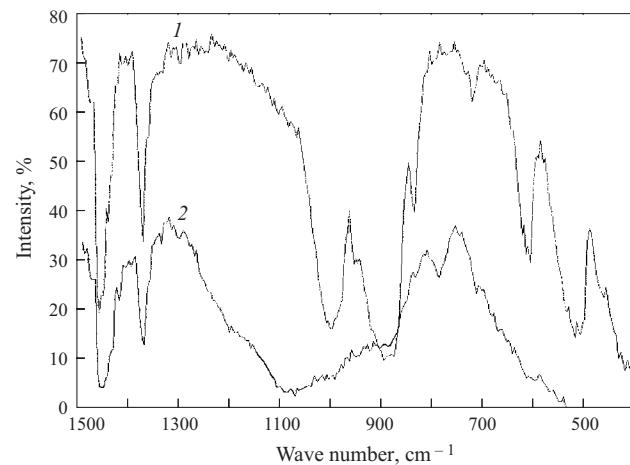
The effect of the silica-containing component on the formation of forsterite is revealed by analyzing the behavior of the xerogel based on magnesium citrate (Fig. 1). The use of  $SiO_2$  sol as the silica-bearing component results in the “freezing” of the forsterite formation process. This is indicated by the absence of the exothermic effect corresponding to forsterite-formation on the DTA curve. This agrees well with the data of the petrographic analysis, which indicates that at 600°C the initial components decompose with the formation of a small amount of phases transitional to forsterite, and only a series of solid solutions based on forsterite is formed at 1200°C. All this is due not only to the higher temperature of magnesium citrate decomposition but also to the



**Fig. 2.** Temperature dependence of the specific surface area of forsterite powder synthesized from  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  and SF (1),  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  and SF (2),  $\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$  and SF (3),  $\text{Mg}_3(\text{C}_6\text{H}_5\text{O}_7)_2$  and SF (4), and  $\text{Mg}_3(\text{C}_6\text{H}_5\text{O}_7)_2$  and  $\text{SiO}_2$  sol (5).

type of the silica-containing component, since the disperse phase of the sol is mainly represented by cristobalite crystals and not by amorphous particles as in the case of the silica filler. Furthermore, a high value of the specific surface area ( $46.24 \text{ m}^2/\text{g}$ ) characterizes precisely the process of decomposition of the initial components at  $600^\circ\text{C}$  (Fig. 2) and not the specific surface area of forsterite (thus, at  $800^\circ\text{C}$  the specific surface area abruptly decreases and is equal to  $7.37 \text{ m}^2/\text{g}$ ). With an increasing heat-treatment temperature, the specific surface area of the powder decreases, regardless of the type of initial components, which is primarily related to the recrystallization process.

For a more precise identification of the composition of the emerging phases, the IR spectra of the powders were recorded, which corroborated the data obtained by other methods. The IR spectra of forsterite exhibit two main absorption bands: at  $1000 - 1100$  and around  $900 \text{ cm}^{-1}$ , which become more clearly expressed with increasing synthesis temperature. This is a general tendency that indicates the formation of magnesium orthosilicate with isolated tetrahedrons  $[\text{SiO}_4]$ . It should be noted that the absorption bands are registered at different temperatures for different initial compounds, and their intensity is not equal: for the forsterite synthesized from magnesium acetate the bands are observed at  $600^\circ\text{C}$  (Fig. 3), for the forsterite synthesized from magnesium chloride, sulfate, and citrate — at  $800^\circ\text{C}$ , and from nitrate — at  $1000^\circ\text{C}$ . Only in the forsterite obtained from mag-



**Fig. 3.** IR absorption spectra of forsterite powder based on  $\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$  and SF, calcination temperature  $600^\circ\text{C}$  (1), and  $\text{Mg}_3(\text{C}_6\text{H}_5\text{O}_7)_2$  and  $\text{SiO}_2$  sol, calcination temperature  $1200^\circ\text{C}$  (2).

nesium citrate and  $\text{SiO}_2$  sol are the absorption bands extremely blurred even at  $1200^\circ\text{C}$ .

Consequently, the type of the initial compounds of magnesium and silicon has a significant effect on the course of the reaction and its completion, the starting temperature of the forsterite formation, and the homogeneity of the crystal sizes. When using magnesium chloride, sulfate, citrate, and especially nitrate, the formation of forsterite is less intense and proceeds at higher temperatures than the standard ones for this technology. The use of magnesium acetate significantly lowers the starting temperature of the forsterite formation. Thus, an active formation of forsterite starts already at a temperature of  $600^\circ\text{C}$ . It should be noted that the amorphous forms of silica are preferable for use as the silica-bearing component to the crystalline forms of silica.

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